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Optimization of Synthesis Conditions for LiFePO₄/C Nanocomposites by Dimethyl Sulfoxide Assisted Solution-Phase Method

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Olivine-type LiFePO₄ is synthesized by a solution-phase method, using dimethyl sulfoxide (DMSO) as a boiling point raiser and crystal growth inhibitor under ambient pressure and low temperature for a short time. The crystalline structure and morphology of the composites are characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. By analyzing the ratio of solvent to water, reactant concentration, reaction time, sintering time, and temperature we determine the optimal conditions for synthesizing LiFePO₄/C nanocomposites, which are as follows: DMSO:water = 1:1, reactant concentration 1 M, reaction time 2 h, mixed with a certain amount of glucose and sintered at 600°C under a 5% H₂–95% N₂ atmosphere for 3 h. The LiFePO₄/C thus prepared has a well developed olivine-type structure, small crystals, and a narrow size distribution. Electrochemical performance tests show that the special capacity of LiFePO₄/C at discharge rates of 0.2 C and 1 C is 157.7 mAh g⁻¹ and 142.5 mAh g⁻¹, respectively. A special capacity of 126 mAh g⁻¹ at 5 C and 104 mAh g⁻¹ at 10 C is even achievable, with no significant capacity fading after 200 cycles, and the material delivers a good high-rate discharge property and excellent cycling performance. © 2012 The Electrochemical Society. [DOI: 10.1149/2.004204jes] All rights reserved.

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LiFePO₄ is regarded as a promising cathode material for lithium ion batteries due to its high theoretical capability (170 mAh g⁻¹), stable discharge platform (3.4 V), relatively low cost, excellent heat stability, low toxicity, reasonable safety, and good structural stability.^{1–3} However, LiFePO₄ has two main defects: slow lithium ion diffusion across the LiFePO₄/FePO₄ interface and low electronic conductivity, which leads to poor high-rate discharge performance.^{4,5} Previously, two approaches have been reported to address these defects. One is to improve Li⁺ ion diffusion by doping with Mg, Mn, V, and Ti to reduce the particle size.^{6–10} The other is to improve electrical conductivity by coating the LiFePO₄ particle surface with amorphous carbon, and nanosized Ag and Cu.^{11–14} Recent studies show that reducing the size of LiFePO₄ can shorten the lithium ion diffusion channel in the solid phase, which is beneficial for the intercalation and deintercalation of lithium ions; this is very important for improving the high-rate discharge property.^{2,15,16} To date, many different methods have been developed to synthesize LiFePO₄ with fine, uniform particles, including sol-gel routes,¹⁷ co-precipitation,¹⁸ spray drying,¹⁹ and so on. Although these methods can improve the degree to which the materials are mixed, the process of drying the precursor is complicated and the product still requires lengthy heat-treatment. Recently, some researchers have proposed synthesizing LiFePO₄ nanocomposites in the pure liquid phase, such as by hydrothermal/solvothermal processes.^{20–24} Ou et al.²⁵ synthesized LiFePO₄ through a hydrothermal reaction using FeSO₄ · 7H₂O, H₃PO₄, and LiOH · H₂O as the starting materials at 180°C for 6 h, followed by sintering at 750°C under a 5% H₂–95% N₂ atmosphere for 6 h. The prepared sample had a particle size of 0.5–1 μm and exhibited a discharge capacity of 154 mAh g⁻¹ at 0.2 C and 136 mAh g⁻¹ at 5 C. Hong et al.²⁶ synthesized LiFePO₄ using a continuous supercritical hydrothermal method at 25 MPa and 400°C under various flow rates over a short time. The obtained samples had a grain dimension range of 200–800 nm, and the capacity declining rates were less than for LiFePO₄/C synthesized using the solid-state method. Rangappa et al.²⁷ developed a new route for the synthesis of LiFePO₄/C nanocrystals (<15 nm) by an organic molecules assisted supercritical water process. They mixed FeC₂O₄ · 2H₂O, NH₄H₂PO₄, LiOH, and ascorbic acid, then stirred the mixture well in a beaker for 1 h. The precursor solution was charged in a stainless steel reactor and heated up to 400°C at

40 MPa for 10 min, quenched with cold water, then heated at 500°C for 2 h in a N₂ and H₂ atmosphere. The obtained samples showed a theoretical capacity of LiFePO₄ of about 97% and very good cyclic performance. Although particle size can be controlled by hydrothermal means, which shortens the reaction time, the process needs to start at high temperature and pressure, which is challenging for industrial production. Delacourt et al.²⁸ kept a mixture of FeSO₄ · 7H₂O, H₃PO₄, and LiOH · H₂O under refluxing conditions for 16 h under magnetic stirring, then annealed the precipitate for 3 h at 500°C under a N₂/H₂ gas flow. The LiFePO₄ obtained by this method had small particles and a very narrow particle size distribution, and exhibited very satisfactory electrochemical properties in terms of specific capacity and capacity retention upon cycling. This reaction was carried out in the liquid phase under ambient pressure and low temperature, but the reaction time was too long. Delacourt et al.²⁹ suggested that in the solution phase, using ethylene glycol, dimethyl sulfoxide (DMSO) and N-methyl formamide as co-solvent is facilitating to the formation of LiFePO₄ nanoparticles.

In our previous work,³⁰ we successfully synthesized the sphere-like LiFePO₄/C nanocomposites by the solution-phase method, in which LiFePO₄ nanoparticles were prepared by using DMSO as a boiling point raiser and crystal growth inhibitor at 108°C and ambient pressure for a short time. Actually, the electrochemical performances of electrodes depend on many factors, such as the reaction temperature and time, reactant concentration, the ratio of DMSO to water and the sinter temperature and time, which have great effects on their performances. Up to date, there has hardly report on the synthesis of LiFePO₄ by the solution-phase method at ambient pressure and low temperature. To determine the optimal conditions for synthesis of LiFePO₄/C, this paper presents a systematic study in consideration of above factors.

Experimental

The LiFePO₄ preparation process was as follows. DMSO was added to an equimolar solution of FeSO₄ · 7H₂O and H₃PO₄. LiOH · H₂O was gradually added to bring the pH of the mixture to 7, yielding a final Li:Fe:P molar ratio of about 3:1:1. Then, the mixed solution was heated up to ebullition and reacted at the boiling point for 1–5 hours in a reflux device under the protection of a nitrogen atmosphere, then cooled to room temperature and filtered; the precipitate was washed with distilled water several times and dried

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Table I. Boiling points of solution with different ratios of DMSO to water.

DMSO:H ₂ O	0.5:1	1:1	2:1
boiling points/°C	104	108	113

in a vacuum drying oven at 120°C for 4 h, then sieved to obtain LiFePO₄.

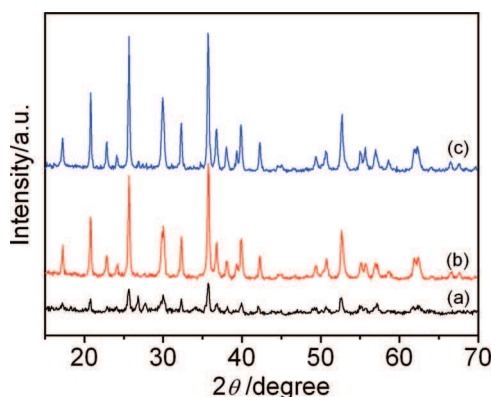
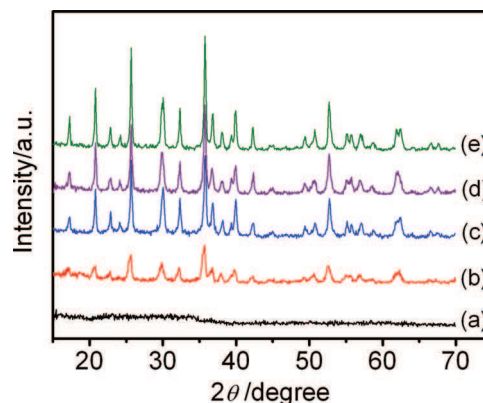
LiFePO₄/C nanocomposites (3.5% carbon content) were synthesized by the following steps. The LiFePO₄ powder was mixed with a certain amount of glucose, then sintered in a pipe furnace under a 5% H₂–95% N₂ atmosphere. After heating, grinding, and sieving, LiFePO₄/C nanocomposites were obtained.

Electrochemical characterization was performed on the prepared electrodes as follows. A mixture of LiFePO₄, carbon black, and polyvinylidene fluoride (PVDF) in a given ratio (85:10:5) was ground in an agate mortar, then *N*-methyl-2-pyrrolidone (NMP) was added to the mixture under continuous stirring. The obtained slurry was spread on an aluminum current collector, dried at 120°C for 12 h under a vacuum atmosphere (−0.1 MPa), then pressed to form a cathode electrode. CR2016 coin cells were assembled in an argon-filled glove box in which oxygen and water were kept below 2 ppm. Lithium metal was used as the anode and a 1 M solution of LiPF₆ in EC:DEC (1:1, v/v) was used as the electrolyte. The cells were tested on a Land CT2001A battery tester at room temperature.

Results and Discussion

Effect of the ratio of DMSO to water.— Because DMSO plays the role of boiling point raiser and crystal growth inhibitor in the reaction, LiFePO₄ can be obtained under ambient pressure and low temperature. During our experimental process we found that the boiling point of the mixed solution changed with different proportions of DMSO and water.

As shown in Table I, the solution's boiling point rises as the ratio of DMSO to water increases. Fig. 1 shows the XRD patterns of LiFePO₄ obtained using different ratios of DMSO to water. It can be seen that the solution temperature has a great influence on the crystallinity of the products. When the ratio of DMSO to water is 1:2, the relative boiling point of the solution is 104°C and the diffraction peak intensity is weak, which indicates poor crystallinity. As the ratio of DMSO to water increases, the boiling point of the solution rises and the diffraction peak intensity becomes stronger. All the diffraction peaks of sample b and sample c can be attributed to lithium iron phosphate (JCPDS Card no. 40-1499), no impurity peaks are observed, and the intensities of the diffraction peaks are stronger, indicating that the

**Figure 1.** XRD patterns of LiFePO₄ obtained using different ratios of DMSO to water: (a) 1:2, (b) 1:1 and (c) 2:1.**Figure 2.** XRD patterns of product obtained at different reaction concentrations: (a) 0.1 M, (b) 0.25 M, (c) 0.5 M, (d) 0.75 M, and (e) 1.0 M.

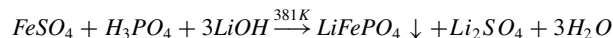
reaction for the formation of LiFePO₄ can be carried out above a certain temperature. Taking crystallinity and cost into consideration, the optimal ratio of DMSO to H₂O is 1:1.

Effect of reactant concentration.— When the ratio of DMSO and mixed water solution was fixed at 1:1, the boiling point of the mixed solution reached 108°C. Fixing the reaction time at 2 h, we can examine the effect of reactant concentration on the crystalline structure of the products.

Fig. 2 shows the XRD patterns of products obtained at different reaction concentrations. It can be seen that when the reactant concentration of FeSO₄ is 0.1 M, the obtained product is completely amorphous, indicating that the crystallization reaction did not occur at a concentration below 0.1 M. The characteristic diffraction peaks of LiFePO₄ gradually appear and the intensity of the peaks gradually increases with increasing reactant concentration. When the reactant concentration of LiFePO₄ increases to 1 M, the diffraction peaks are sharp and narrow, indicating that the sample had high crystallinity. After retrieval, all the diffraction peaks are in full accord with the ordered LiFePO₄ olivine structure (JCPDS Card no. 40-1499) indexed in the orthorhombic *Pnma* space group and show no evidence of impurity phases. Experiments indicated that olivine-structured LiFePO₄ can be directly synthesized in a mixture of DMSO and water under ambient pressure and low temperature for a short time. A high concentration is favorable to crystal structure development and improved production efficiency. Due to the poor solubility of LiOH, a 1 M reactant concentration is identified to be favorable.

Effect of reaction time.— The ratio of DMSO and water solution was fixed at 1:1, and the reactant concentration of FeSO₄ was fixed at 1 M. The influence of reaction time on the crystal structure and particle sizes of the product was then examined.

The XRD patterns and SEM images of LiFePO₄ obtained for different synthesis times are shown in Fig. 3a. In each case, the XRD patterns of all samples accord very well with LiFePO₄ and no impurity phase can be detected. It can be concluded that olivine-structured LiFePO₄ can be synthesized in a mixture of DMSO and water at 108°C in only 1 h. This process can be expressed by the following equation:



The key factor in the formation of LiFePO₄ using this system is the boiling point rise caused by DMSO, which can reduce the surface tension of the initial LiFePO₄ crystalline nucleus and impel the reaction toward the formation of LiFePO₄. In Figure 3 it can be seen that as the reaction time is prolonged, the crystallinity and particle sizes all gradually increase. The particles are smaller with a 1 h reaction time, but the crystallinity is lower. While the particle size increases significantly after 4 h, this length of time is unfavorable to the intercalation and deintercalation of lithium ions. The LiFePO₄

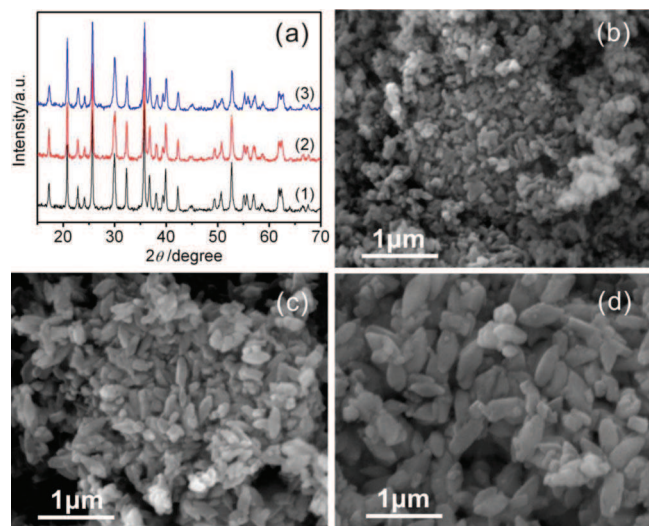


Figure 3. (a) XRD patterns of LiFePO_4 obtained with different synthesis times: (1) 1 h, (2) 2 h, and (3) 4 h, and their corresponding SEM images for (b) 1 h, (c) 2 h, and (d) 4 h.

obtained in 2 h has a well developed crystal structure, small crystals, and a narrow size distribution, so we conclude that 2 h is the best reaction time for preparing LiFePO_4 .

Effect of sintering time.— Although LiFePO_4 with an olivine-type structure and small grains can be synthesized in a mixed solution of DMSO and H_2O in a short time, its electrochemical performance is unsatisfactory, especially the rate capability. According to Delacourt et al.,²⁸ this may be attributable to the presence of Fe^{3+} in the crystal structure of LiFePO_4 obtained by the liquid-phase method and the hydrothermal method, which can be expressed as $\text{LiFe}_{1-x}\text{Fe}_x\text{PO}_4(\text{OH})_x$, so appropriate heat-treatment is important. There are two problems to consider in heat-treatment: guaranteeing the purity and crystallinity of samples, and maintaining the particle sizes and size distribution of samples synthesized in the liquid-phase. For this reason, we mixed the as-prepared LiFePO_4 powder with a certain amount of glucose and sintered the mixture under a 5% H_2 –95% N_2 atmosphere. Part of the amorphous carbon formed by glucose at a high temperature is used to reduce Fe^{3+} while the rest coats the surface of the LiFePO_4 , functioning as a conductor and inhibiting grain growth.

The crystalline structure and morphology of the LiFePO_4/C powders sintered at 600°C for 1 h, 3 h, and 5 h can be observed in Fig. 4. It can be seen that as sintering time increases, the crystallinity and particle sizes of the samples increase. The LiFePO_4/C sintered at 600°C for 3 h has intact, higher diffraction peaks and fine crystals in the range of 80–300 nm with a narrow particle size distribution. Increasing the sintering time to 5 h results in an intact crystalline structure and large particles that prevent the intercalation and deintercalation of lithium ions. Shortening the sintering time to 1 h weakens the intensity of the diffraction peaks too much. Thus, the most feasible sintering time proposed is 3 h.

Effect of sintering temperature.— To determine the optimal sintering temperature, LiFePO_4/C was obtained after annealing at 500°C , 600°C , and 700°C for 3 h. XRD patterns and SEM images of LiFePO_4/C obtained at different sintering temperatures are shown in Fig. 5. We can see that the sample calcined at 600°C has intact, higher diffraction peaks and fine crystals in the range of 80–300 nm with a narrow particle size distribution. When the sintering temperature is increased to 700°C , the particle size increases. Reducing the sintering temperature is favorable for preventing particle growth but

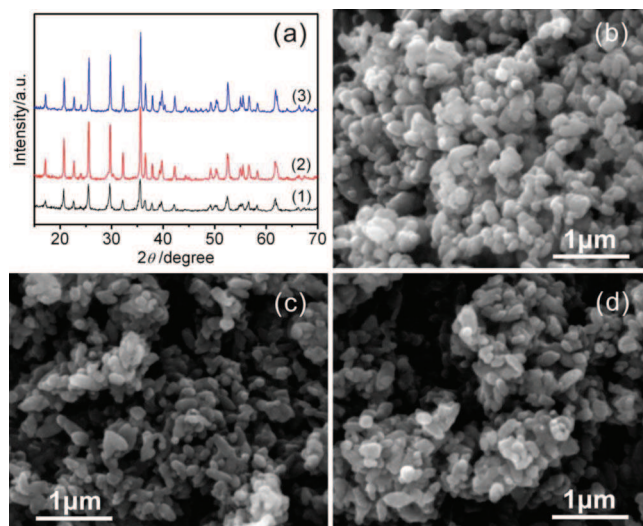


Figure 4. (a) XRD patterns of LiFePO_4/C obtained by annealing at 600°C for (1) 1 h, (2) 3 h, and (3) 5 h, and their corresponding SEM images for (b) 1 h, (c) 3 h, and (d) 5 h.

unfavorable for crystallinity. Therefore, the trade-off feasible sintering temperature is 600°C .

Electrochemical properties.— The electrochemical performance of the synthesized LiFePO_4/C depended strongly on the sintering temperature and time. The optimal LiFePO_4/C was sintered at 600°C for 3 h, and had a first discharge capacity of 157.7 mAh g^{-1} at 0.2 C , which is close to 93% of the theoretical capacity (170 mAh g^{-1}). The initial discharge capacity of LiFePO_4/C first increased then decreased with increasing time (Fig. 6a) and temperature (Fig. 6b). This result can be attributed to the optimal particle size and crystallinity, which were confirmed by the XRD and SEM patterns.³¹ However, the length of the voltage platform is found to be less than that of sample treated for 5 h. And at the same time, the arc portion at the end of curve is longer. It might be attributed to the formation of defect sites during annealing process according to other reports.^{32,33} As shown in Fig. 4a, the XRD patterns of LiFePO_4 with different sintering times at 600°C ,

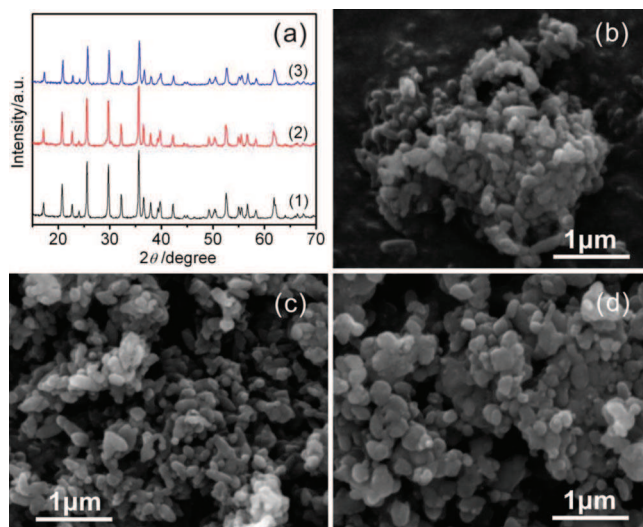


Figure 5. (a) XRD patterns of LiFePO_4/C obtained by annealing at (1) 500°C , (2) 600°C , and (3) 700°C for 3 h, and their corresponding SEM images at (b) 500°C , (c) 600°C , and (d) 700°C .

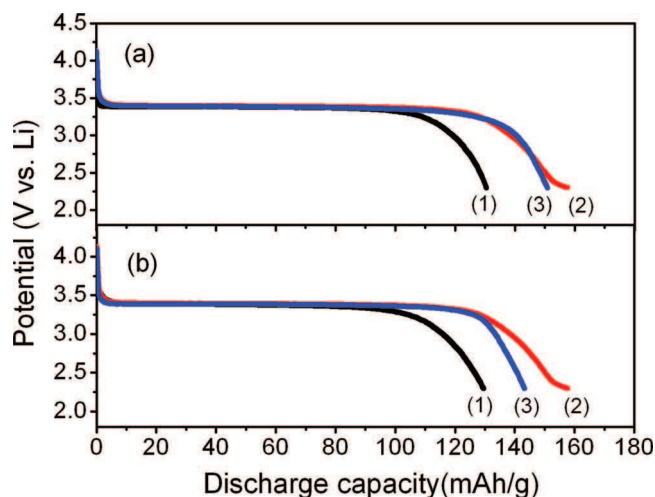


Figure 6. (a) Discharge curves of LiFePO₄/C nanocomposites for different sintering times: (1) 1 h, (2) 3 h, and (3) 5 h; (b) discharge curves of LiFePO₄/C nanocomposites at different sintering temperatures: (1) 500°C, (2) 600°C, and (3) 700°C.

the crystallinity of sample treated for 5 h is higher than that of sample treated for 3 h. In the meantime, the crystallinity improves with the increase in sintering temperature. According to some references, electrodes with low crystallinity might have nanoclusters or defect sites, which make the non-uniform lithiation or delithiation occur during the cycling.^{32,33} This might be the reason of somewhat declining plateau in the sample treated for 3 h.

Figure 7 shows the initial discharge curves of LiFePO₄/C prepared under optimal conditions between 2.3 and 4.2 V at different rates. The first discharge capacity is 157.7 mAh g⁻¹ at 0.2 C, close to 93% of the theoretical capacity (170 mAh g⁻¹). Good discharge platforms are still maintained even at discharge rates of 0.5 C, 1 C, 3 C, and 5 C, with first discharge capacities of 149 mAh g⁻¹, 142.5 mAh g⁻¹, 129.5 mAh g⁻¹, and 126.5 mAh g⁻¹, respectively. Even at 10 C, the discharge specific capacity of the product reaches 104 mAh g⁻¹, demonstrating a good high-rate discharge property. The results indicate significant potential for meeting the requirements of electric vehicles (EVs) and hybrid electric vehicles (HEV).

The cycling behavior of LiFePO₄/C prepared under optimal conditions at room temperature was presented in Figure 8. There the capacity retention rate remains above 90% of the initial rate after 200 cycles at 5 C and 10 C. These results demonstrate that the LiFePO₄/C

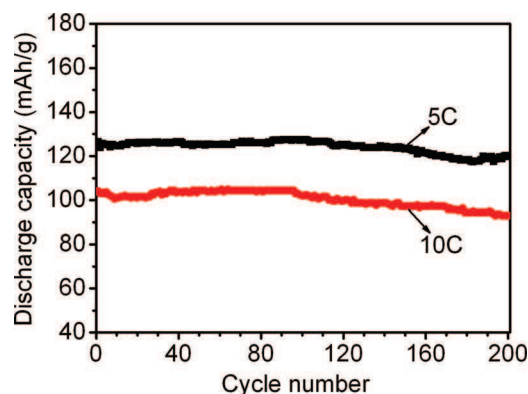


Figure 8. Cycling performance of LiFePO₄/C prepared under optimal conditions, tested at room temperature.

nanoparticle cathode materials prepared by the liquid-phase method in this study exhibit excellent discharge capability and good high-rate cycling. Thus, the material's exceptional electrical properties first arise from the small, uniform LiFePO₄/C nanoparticles obtained by the liquid-phase method, then from carbon encapsulation and spheroidization.

The above experiments show that the particle size of LiFePO₄ has a great effect on its charge-discharge capacity, especially its rate capability.¹⁶ When the grains are smaller, their surfaces can be effectively improved to increase their contact area with the electrolyte and shorten the lithium ion diffusion channel, which is beneficial for the insertion and extraction of lithium ions.³⁴ Meanwhile, the presence of a small amount of carbon can also increase the material's conductivity. Zhang³⁵ indicated that LiFePO₄ with a particle size of 100~350 nm showed better electrochemical performance at high rates than excessively small LiFePO₄ (less than 100 nm). The particle size of our LiFePO₄/C composite is in the range of 80~300 nm, so the improvement in high rate capability is in accordance with Zhang et al.

Conclusions

In this paper, we firstly synthesized olivine-type LiFePO₄ by the solution-phase method using DMSO as a boiling point raiser and crystal growth inhibitor at low temperature and ambient pressure for a short time, and then sintered the LiFePO₄ with a certain amount of glucose to get LiFePO₄/C composite. Through observing the effects of the solvent to water ratio, reactant concentration, reaction time, and sintering temperature on the crystallinity, morphology, and electrochemical performance of the LiFePO₄/C composites, we found the optimal conditions to be as follows: DMSO:water = 1:1, reactant concentration 1 M, reaction time 2 h, mixed with a certain amount of glucose and sintered at 600°C under a 5% H₂-95% N₂ atmosphere for 3 h. The LiFePO₄/C composites obtained by this method and condition deliver smaller, more uniform particles and better electrochemical performance. Electrochemical tests showed that the special capacity of LiFePO₄/C composite is 157.7 mAh g⁻¹ at a 0.2 C discharge rate, close to 93% of the theoretical capacity (170 mAh g⁻¹). A special capacity of 126 mAh/g and 104 mAh/g can be achieved even at 5 C and 10 C, with the material showing no significant capacity fading after 200 cycles. The results demonstrate that the LiFePO₄/C composites synthesized by this method have a high specific capacity and excellent cycling stability and rate capability.

Acknowledgments

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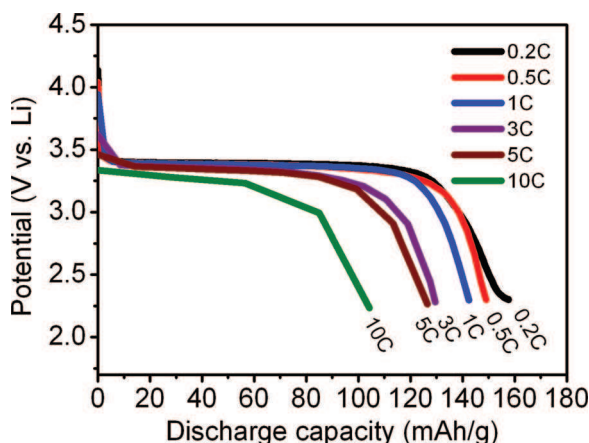


Figure 7. Discharge curves of LiFePO₄/C prepared under optimal conditions, at different rates.

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